

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	30 October 1996	Technical	
4. TITLE AND SUBTITLE  SYNTHESIS OF A NOVEL INDIUM-NITROGEN CAGE COMPOUND. MOLECULAR STRUCTURE OF [NpIn(M-(NH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] <sub>4</sub> (Np = CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> )		5. FUNDING NUMBERS  •N00014-95-1-0194 R&T Project 3135008---16 •Dr. Harold E. Guard	
6. AUTHOR(S)  Hamid Rahbarnoohi and Richard L. Wells, and Arnold L. Rheingold		8. PERFORMING ORGANIZATION REPORT NUMBER  Technical Report No. DU/DC/TR-62	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Department of Chemistry Duke University Durham, NC 27708-0346		9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research 300 North Quincy Street Arlington, VA 22217-5000	
11. SUPPLEMENTARY NOTES  Accepted for publication in <i>J. Chem. Soc, Chem. Commun.</i>		10. SPONSORING/MONITORING AGENCY REPORT NUMBER  19961209 037	
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for Public Release Distribution Unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Reaction of the ligand 1,2-(NH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> with InNp <sub>3</sub> (Np = neopentyl = CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ) afforded the tetrameric compound [NpIn(μ-(NH) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] <sub>4</sub> which contains five-coordinate indium centers having square pyramidal geometry and an overall approximate tetrahedral symmetry.			
14. SUBJECT TERMS  indium, nitrogen, cage compound, structure		15. NUMBER OF PAGES  9	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE  Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT  Unclassified	20. LIMITATION OF ABSTRACT  Unlimited

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194  
R&T Project 3135008---16

Dr. Harold E. Guard

Technical Report No. DU/DC/TR-62

**SYNTHESIS OF A NOVEL INDIUM-NITROGEN CAGE COMPOUND.  
MOLECULAR STRUCTURE OF [NpIn(M-(NH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>4</sub> (Np = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>)**

H. RAHBARNOOHI,<sup>1</sup> R. L. WELLS,<sup>1</sup> AND A. L. RHEINGOLD<sup>2</sup>

<sup>1</sup>Department of Chemistry, Duke University, Durham, NC 27708

<sup>2</sup>Department of Chemistry, University of Delaware, Newark, DE 19716

Accepted for publication in *J. Chem. Soc. Chem Commun.*

Duke University  
Department of Chemistry,  
P. M. Gross Chemical Laboratory  
Box 90346  
Durham, NC 27708-0346

30 October 1996

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

Synthesis of a novel indium-nitrogen cage compound. Molecular structure  
of  $[\text{NpIn}(\mu\text{-}(\text{NH})_2\text{C}_6\text{H}_4)]_4$  ( $\text{Np} = \text{CH}_2\text{C}(\text{CH}_3)_3$ )

Hamid Rahbarnoohi,<sup>a</sup> Richard L. Wells,<sup>\*a</sup> and Arnold L. Rheingold<sup>b</sup>

<sup>a</sup> Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University,  
Durham, North Carolina 27708, U.S.A.

<sup>b</sup> Department of Chemistry, University of Delaware, Newark, Delaware 19716, U.S.A.

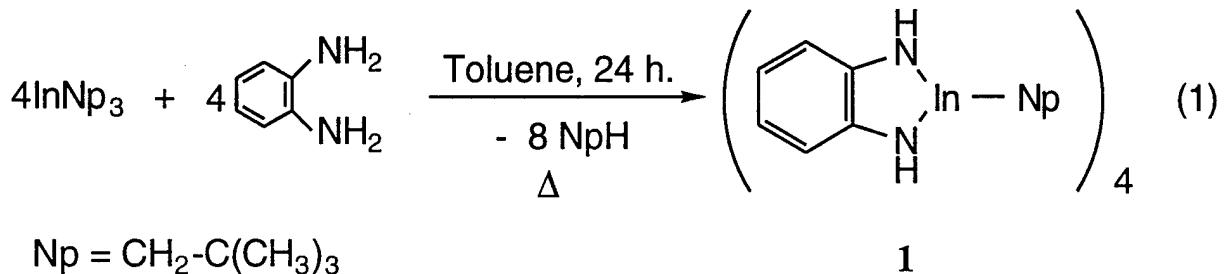
Reaction of the ligand  $1,2(\text{NH}_2)_2\text{C}_6\text{H}_4$  with  $\text{InNp}_3$  ( $\text{Np} = \text{neopentyl} = \text{CH}_2\text{C}(\text{CH}_3)_3$ ) afforded the tetrameric compound,  $[\text{NpIn}(\mu\text{-}(\text{NH})_2\text{C}_6\text{H}_4)]_4$ , which contains five-coordinate indium centers having square pyramidal geometry and an overall approximate tetrahedral symmetry.

---

\*Author for correspondence

Chelating ligands containing the donor atoms of Group 15 have been used for stabilizing the electrophilic Group 13 elements.<sup>1-3</sup> The relevant studies have shown the diversity of such compounds characterized by varied degrees of oligomerization and complex coordination of the metal centers. In this regard, the five-coordinated organometallic compounds of Group 13 elements were limited to those using macrocyclic ligands.<sup>4</sup> For example, most of the five-coordinated indium compounds usually have distorted bipyrimidal<sup>5-7</sup> geometry, while fewer are known to have square pyramidal geometry.<sup>8-10</sup> In a recent study, we demonstrated that the independent reactions of AlMe<sub>3</sub> and GaMe<sub>3</sub> with 1,2(EH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (E = N, P) in a 2:1 ratio produces four-coordinate tetrametallic compounds,  $\{(Me_2M)_4[(\mu\text{-PH})_2(C_6H_4)]_2\}$  (M = Al, Ga), through alkane elimination.<sup>11</sup> In a related study, reactions of sterically demanding primary amines with AlMe<sub>3</sub> resulted in isolation of several novel large aggregates of aluminum compounds but similar reactions with GaMe<sub>3</sub> led to C-H activation, forming "cyclometallated" compound.<sup>12</sup> Only recently, Roesky<sup>13</sup> and co-workers reported the first organometallic cubane compounds for GaN and InN systems, (C<sub>6</sub>F<sub>5</sub>NMMe)<sub>4</sub> (M = Ga, In), from the reaction of MMe<sub>3</sub> with C<sub>6</sub>F<sub>5</sub>NH<sub>2</sub>. Herein, we discuss the formation of the novel 12-member cluster, [NpIn( $\mu$ -(NH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)]<sub>4</sub> (Np = neopentyl = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>).

The reaction of  $\text{InNp}_3$  with  $1,2(\text{NH}_2)_2\text{C}_6\text{H}_4$  in a 1:1 ratio resulted in isolation<sup>‡</sup> of **1** as shown in equation 1.



Compound **1** is formed via alkane elimination and is isolated as colorless crystals which are sparingly soluble in aromatic solvent and slowly decompose in the presence of air. The X-ray structural analysis<sup>8</sup> of **1** reveals a tetramer with overall tetrahedral symmetry, which is composed of square pyramidal indium centers with similar In-N distances. The In1/In1A and In1B/In1C have closer In···In interaction than the other pairs. The N···N separation between N2/N2A and N2B/N2C is 2.74 Å which is shorter than distances between N1A/N1B and N1/N1C (3.19 Å). This is the result of the members of the pair being doubly bridged by the N2 atoms. All four In atoms are physically and chemically equivalent, but there is not a four fold overall symmetry. The In-N distances are between 2.259(6) and 2.290(6) Å (average 2.276(6) Å) and are slightly longer than the cubane, (C<sub>6</sub>F<sub>5</sub>NInMe)<sub>4</sub>, with the average In-N bond length of 2.20 Å.<sup>13</sup> This can be rationalized since the indium atoms in **1** are five-coordinated and in (C<sub>6</sub>F<sub>5</sub>NInMe)<sub>4</sub> are tetrahedral. In conclusion, the alkane elimination works smoothly to yield **1** and we will now investigate whether aluminum and gallium can form large clusters with 1,2(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.

**Acknowledgment.** We are grateful for the financial support of this work provided by the Office of Naval Research.

#### Footnotes

† **General Considerations.** All manipulations were performed using general Schlenk and dry box techniques. Solvents were dried over Na/K alloy and distilled under dinitrogen prior to use. Literature method was used to prepare In(CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>.<sup>14</sup> 1,2(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> was purchased from Aldrich and used as received. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}NMR spectra were recorded on a GE-300 spectrometer operating at 300 and 75.4 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively. Melting point (uncorrected) was obtained with a Thomas-Hoover Uni-melt apparatus and capillary

was flame-sealed under argon. Elemental Analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Mass spectrum data was collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. IR Spectrum were acquired for KBr pellet on a BOMEM Michelson MB-100 FT-IR spectrometer. X-ray crystallographic data was obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation.

<sup>‡</sup> **Synthesis of 1.** Inside the Dri-Lab, 0.71 g (2.17 mmole) of InNp<sub>3</sub> was combined with 0.24 g (2.17 mmole) of 1,2(NH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> in a 250 ml Schlenk flask and ca. 40 ml of toluene was added to the mixture. The mixture was refluxed for 24 h. The volume of resultant pale-yellow solution was decreased by ca. 20 ml in *vacuo* and left undisturbed. The X-ray quality crystals of **1** were deposited in the bottom of flask within 24 h. Yield, 90% based on InNp<sub>3</sub>; mp 245 °C. Anal. Calcd. (Found) for C<sub>44</sub>H<sub>68</sub>N<sub>8</sub>In<sub>4</sub> : C, 45.23 (45.35); H, 5.87 (5.99); N, 9.59 (9.54). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.82(8H, m, C<sub>6</sub>H<sub>4</sub>); 6.66(8H, m, C<sub>6</sub>H<sub>4</sub>); 3.14 (8H, s, N-H); 0.96 (8H, s, In-CH<sub>2</sub>); (36H, s, CMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  142.8, 140.5, 121.2, 119.0, 118.4, 114.3 (s, C<sub>6</sub>H<sub>4</sub>); 34.3 (s, CMe<sub>3</sub>); 31.3 (s, In-CH<sub>2</sub>); 30.9 (s, CMe<sub>3</sub>). Mass spectral data (EI mode): peaks at *m/e*, 293 corresponding to [M<sup>+/4 + H]. IR (cm<sup>-1</sup>) : IR (cm<sup>-1</sup>): 3282, 3310, and 3375 cm<sup>-1</sup>, N-H stretching mode; 1629(w) and 1584(s) cm<sup>-1</sup>, N-H bending mode.</sup>

<sup>§</sup> **X-ray structural solution and refinement.** A suitable crystal was mounted in thin-walled capillaries and sealed with silicone grease under argon atmosphere and then flame-sealed. The unit-cell parameters were obtained by least-squares refinement of the angular setting of 24 reflections ( $20^\circ \leq 2\theta \leq 25^\circ$ ). Preliminary photographic evidence indicated a tetragonal crystal system with 4/m Laue symmetry. The systematic absence in the diffraction data were consistent for I-centering and the following space groups: *I*4, *I*4̄, *I*4/m, *I*422, and *I*4mm, *I*4m2, *I*42m, *I*4/mmm. *E*-statistic suggested a non-

centrosymmetric space group. The presence of tetrahedral molecular symmetry, the absence of mirror plane symmetry in the placement of neopentyl and C<sub>6</sub>H<sub>4</sub> groups, and Z = 2 eliminated all of the space group options except for  $\bar{I}4$ . The solution in  $\bar{I}4$  produced a chemically reasonable structure and computationally stable refinement. The structure was solved by direct method, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. A semi-empirical absorption correction was applied. The structure was refined as a racemic twin with a 70/30 ratio of enantiomeric lattice. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program libraries.<sup>15</sup>

Molecular diagrams showing the solid state conformation and atom numbering schemes of **1** and the core of **1** are presented in Figures 1 and 2, respectively, with selected interatomic distances and angles listed in the figure captions. *Crystal data:* for C<sub>44</sub>H<sub>68</sub>N<sub>8</sub>In<sub>4</sub> (**1**), mw = 1168.34, colorless plate, 0.4 x 0.4 x 0.18 mm, crystal system: tetragonal, space group:  $I\bar{4}$ ,  $a = b = 10.194(2)$  Å,  $c = 23.4380(10)$  Å,  $V = 2435.6(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.593$  g cm<sup>-3</sup>,  $F(000) = 1168$ , MoK $\alpha$  = 0.71073 Å, 2024 reflections collected with 1911 being independent reflections; refinements converged to  $R = 0.0340$  ( $R_{\text{w}}^2 = 0.0894$ ). *Supplementary material:* Atomic coordinates, thermal parameters, complete bond lengths and angles, and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

### References

1. G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds, Volume 1: The Main Group Elements*, Butler & Tanner Ltd. (London), 1967.
2. T. Mole and E. A. Jeffrey, *Organooluminum Compounds*, Elsevier (Amsterdam), 1972.
3. G. H. Robinson, *Coordination Chemistry of Aluminum*, VCH (New York), 1993.
4. J. P. Oliver and R. Kumar, *Polyhedron*, 1990, **9**, 409.
5. M. Khan, R. C. Steevensz, D. G. Tuck, J. G. Noltes and P. W. R. Corfield, *Inorg. Chem.*, 1980, **19**, 3407.
6. R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1982, **21**, 2379.
7. J. R. Leman, H. A. Roman and A. R. Barron, *Organometallics*, 1993, **12**, 2986.
8. D. W. Brown, F. W. B. Einstein and D. G. Tuck, *Inorg. Chem.*, 1969, **8**, 14.
9. P. C. Lecomte, J. Protas, P. Cocolios and R. I. Guilard, *Acta Cryst.*, 1980, **B 36**, 2769.
10. A. M. Arif, D. C. Bradley, D. M. Frigo, M. B. Hursthouse and B. Hussain, *J. Chem. Soc., Chem. Commun.*, 1985, 783.
11. R. L. Wells, H. Rahbarnoohi, P. B. Glazer, L. M. Liable-Sands and A. L. Rheingold, *Organometallics*, 1996, **15**, 3204.
12. K. M. Waggoner and P. P. Power, *J. Am. Chem. Soc.* 1991, **113**, 3385.
13. T. Belgardt, H. W. Roesky, M. Noltemeyer and H. G. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1056.
14. O. T. Beachley Jr., E. F. Spiegel, J. P. Kopasz and R. D. Rogers, *Organometallics*, 1989, **8**, 1915.
15. *SHELXTL PC*, Siemens Analytical X-Ray Instruments, Inc. (Madison, WI), 1990.

**Figure 1.** Molecular diagram (30% probability ellipsoids) of  $C_{44}H_{68}N_8In_4$  (**1**), hydrogen atoms omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (degrees): In(1)-C(1) 2.166(7), In(1)-N(2) 2.270(6), In(1)-N(1) 2.290(6), In(1)-N(1B) 2.259(6), In(1)-N(2A) 2.285(6), N(1)-C(6) 1.453(10), N(2)-C(11B) 1.400(8), C(11)-N(2C) 1.400(8), In(1)…In(1A) 3.2675(10); C(1)-In(1)-N(1B) 119.0(3), C(1)-In(1)-N(2) 119.4(3), N(1B)-In(1)-N(2) 73.8(2), C(1)-In(1)-N(2A) 111.2(3), N(1B)-In(1)-N(2A) 129.0(2), N(2)-In(1)-N(2A) 74.5(2), C(1)-In(1)-N(1) 107.7(3), N(1B)-In(1)-N(1) 89.1(2), N(2)-In(1)-N(1) 132.5(2), N(2A)-In(1)-N(1) 83.9(2), C(6)-N(1)-In(1) 103.4(4), C(6)-N(1)-In(1C) 108.4(4), C(11B)-N(2)-In(1) 112.0(5), C(11B)-N(2)-In(1A) 125.2(4), In(1)-N(2)-In(1A) 91.7(2), In(1C)-N(1)-In(1) 121.7(3).

**Figure 2.** Molecular diagram of the InN core in  $C_{44}H_{68}N_8In_4$  (**1**).

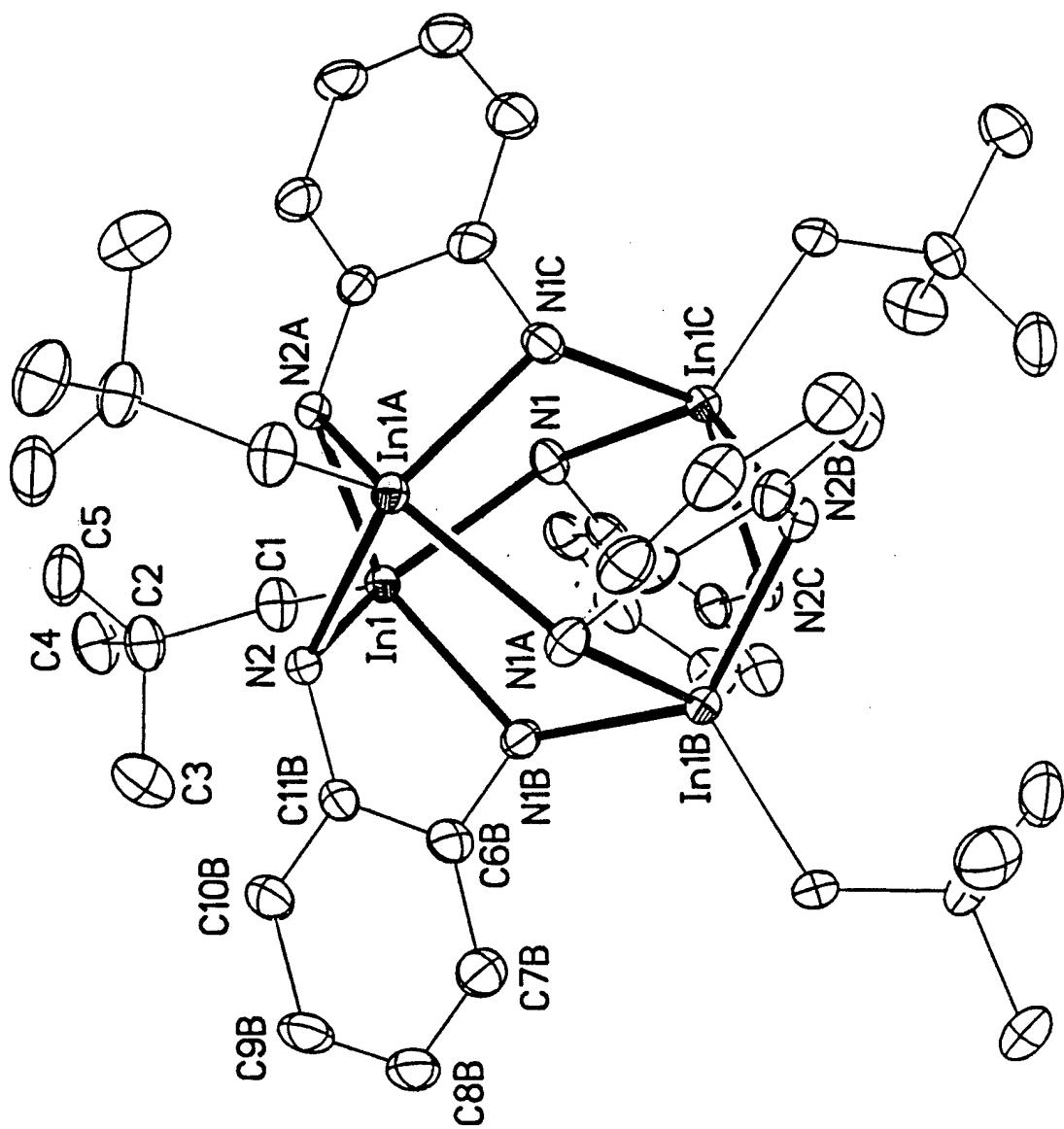


Figure 1

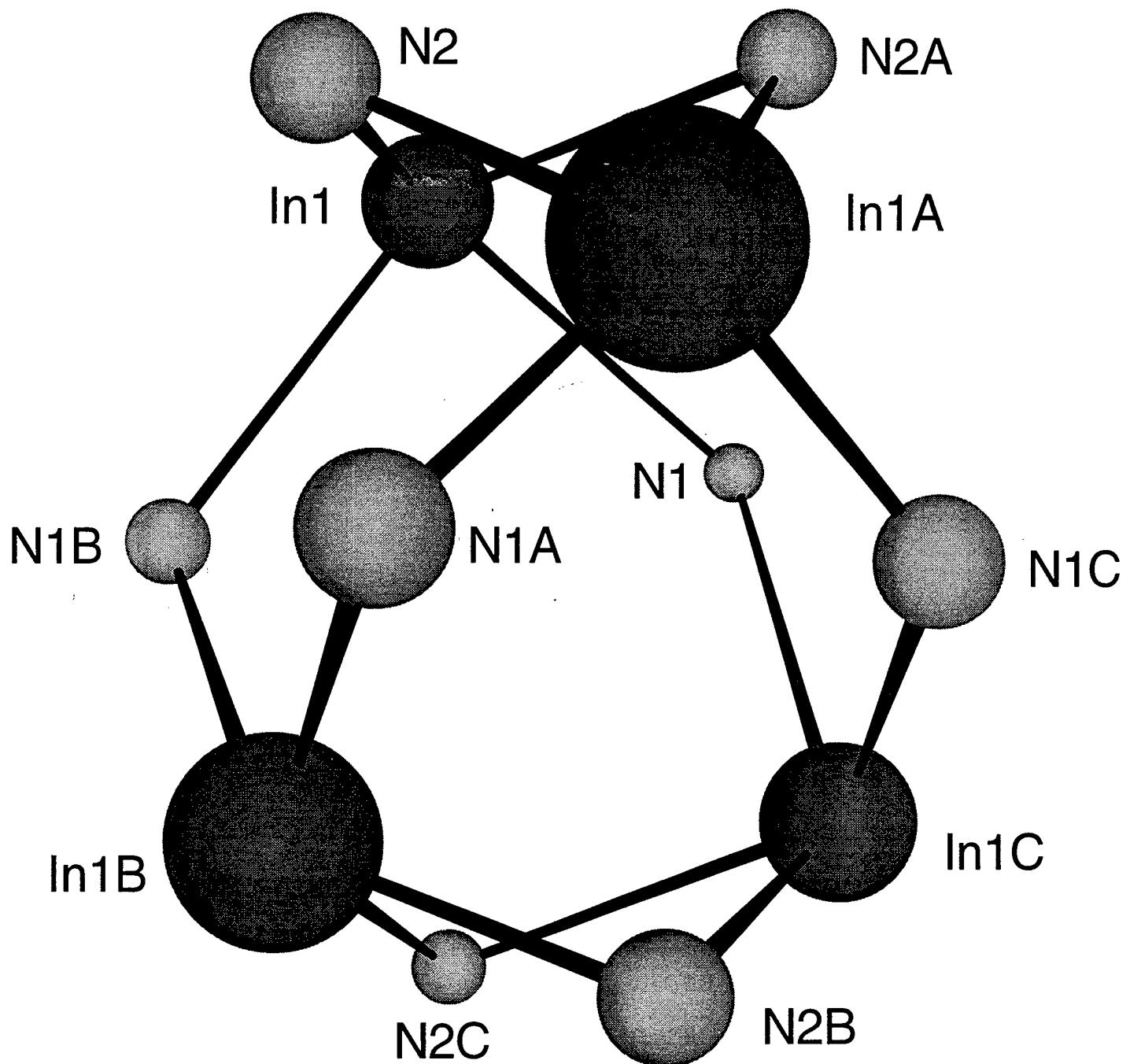


Figure 2

TECHNICAL REPORTS DISTRIBUTION LIST

ORGANOMETALLIC CHEMISTRY FOR ELECTRONIC & OPTICAL MATERIALS

Dr. Harold E. Guard  
Code 1113  
Chemistry Division, 331  
Office of Naval Research  
800 N. Quincy Street  
Arlington, Va 22217-5660

Defense Technical Information  
Center  
Building 5, Cameron Station  
Alexandria, VA 22314

Dr. James S. Murday  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, DC 20375-5320

Dr. John Fischer, Director  
Chemistry Division, C0235  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Richard W. Drisko  
Naval Facilities & Engineering  
Service Center  
Code L52  
Port Hueneme, CA 93043

Dr. Eugene C. Fischer  
Code 2840  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. Bernard E. Douda  
Crane Division  
Naval Surface Warfare Center  
Crane, IN 47522-5000

Dr. Peter Seligman  
Naval Command, Control and  
Ocean Surveillance Center  
RDT&E Division  
San Diego, CA 93152-5000